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DEVELOPMENT OF AN IMPROVED OXYGEN ELECTRODE FOR USE
IN ALKALINE H_2-O_2 FUEL CELLS

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DEVELOPMENT OF AN IMPROVED OXYGEN ELECTRODE FOR USE
IN ALKALINE H_2-O_2 FUEL CELLS

The objective of this project is the synthesis of interstitial compounds for increasing the efficiency of the oxygen electrode in alkaline H_2-O_2 fuel cells. The work is being carried out for the National Aeronautics and Space Administration with Mr. E. M. Cohn as technical monitor. Principal investigators are D. Bienstock, Sayeed Akhtar, C.T. Grein, and Richard C. Diehl.

1136

Bureau of Mines
Pittsburgh Coal Research Center

Quarterly Report for the period ending March 31, 1967

Development of An Improved Oxygen Electrode for Use
in Alkaline H₂-O₂ Fuel Cells

Summary

A total of 41 preparations were synthesized and shipped to Tyco Laboratories in this quarter. These preparations include the carbides and nitrocarbides of the binary alloys Ni-Ag, Co-Ag, and Ni-Co in 3/1, 1/1, and 1/3 weight ratios, and the ternaries Ni-Co-Ag and Ni-Co-Au in a 1/1/1 weight ratio. In addition to the shipments to Tyco Laboratories, 114 samples were sent to 6 other firms engaged in testing these preparations.

An additional two synthesis units are being installed. This will bring the total number of synthesis units to six. Carbiding of metals and alloys is a slow process and each preparation requires 150-200 hours, thus keeping a unit engaged for a week or more on a round-the-clock operation.

Introduction

The object of this project is to develop catalysts for the cathodic reduction of oxygen in alkaline H₂-O₂ fuel cells. The work conducted in cooperation with Tyco Laboratories, Inc., and the materials under investigation are the interstitial compounds of the transition metals and their alloys, with carbon, nitrogen, boron, and silicon. This report deals only with the preparation of these compounds; information on the efficiency of the preparations in laboratory tests may be obtained from the Quarterly Reports of Tyco Laboratories. Samples of the preparations are also sent to other firms designated for the purpose by the technical monitor of N.A.S.A.

Experimental

A. Preparation of Alloys

A modification of the classical method developed by Murray Raney (1) for making skeletal nickel catalysts was employed for the preparation of finely divided alloys of transition metals. The procedure consists of the following steps:

- (1) Melting together of calculated quantities of the metals to be alloyed with an excess of aluminum, in an induction furnace.
- (2) Crushing of the cooled mass to a fine powder.
- (3) Leaching of the powder with an aqueous solution of NaOH to remove aluminum.

The quantities of the components were so adjusted that aluminum amounted to 60 percent of the melt. Silver, gold and palladium used in this work were better than 99.8 percent purity. Commercially obtained Raney alloys of iron, cobalt, and nickel were employed as the source for these metals. The heating chamber of the induction furnace was repeatedly flushed with helium before the furnace was energized. Charges of 125-150 grams at a time were melted in fire clay crucibles.

On cooling most of these Raney alloys were found to be friable and could be easily crushed to a fine powder in a hammer mill or ball mill. Those which were not friable were machined into turnings and then put through the mill to be converted into powder (see fig. 1). The powder was sieved through standard screens and the desired fraction (usually 150-250 mesh) was leached with caustic soda according to the directions of Covert and Adkins (2).

Table 1 is a complete list of the binary and ternary alloys of the transition metals prepared in the laboratory. The x-ray diffraction patterns of the Raney alloys and the leached alloys are under study. A preliminary report on the subject is included separately (see section F).



Melt

Turnings

Powder

FIGURE 1. - Preparation of Powdered Alloy.

TABLE 1.- Alloys of the transition metals prepared
by the Raney method

Raney alloy ^{1/} number	Composition of leached alloy
RA-1 -----	1Ni-1Co
RA-2 -----	1Ni-3Co
RA-3 -----	3Ni-1Co
RA-4* -----	1Ni-3Ag
RA-5* -----	1Ni-1Ag
RA-6* -----	3Ni-1Ag
RA-7* -----	1Co-3Ag
RA-8* -----	1Co-1Ag
RA-9 -----	3Co-1Ag
RA-10* -----	1Ni-1Co-1Ag
RA-11 -----	1Ni-1Co-1Au
RA-12* -----	1Ni-1Ag-1Au
RA-13* -----	1Co-1Ag-1Au
RA-14 (150-400 mesh) -----	1Ni-1Pd
RA-15 (150-400 mesh) -----	1Co-1Pd
RA-16 (150-400 mesh) -----	1Ni-1Co-1Pd
RA-17 (150-400 mesh) -----	1Ni-1Pd-1Au
RA-18 (150-400 mesh) -----	1Fe-1Pd

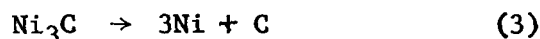
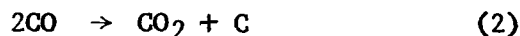
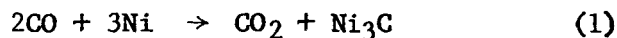
^{1/} Mesh size 150-250 unless otherwise stated.

^{*/} Raney alloys marked with an asterisk were machined into
turnings before crushing.

B. Preparation of Carbides

The finely divided alloys of the transition metals were carbided with carbon monoxide at 250°C. The technique and apparatus employed for carbiding the alloys were the same as described earlier (3) for the preparation of the carbides of iron. Prior to carbiding, each alloy was reduced in a stream of hydrogen at 450°C for 10-20 hours at an hourly space velocity of 1000-2500. The reduced alloy was cooled to 150°-160°C in hydrogen after which the flow gas was changed to carbon monoxide. The temperature of the bed was then raised to 250°C in gradual steps extending over 6-24 hours. This precaution eliminates the risk of a large sudden rise in temperature which causes excessive deposition of free carbon.

The interaction of the alloys of transition metals with carbon monoxide is probably similar to that of nickel with carbon monoxide. The latter system has been studied in considerable detail (4); three distinct reactions are known to proceed concurrently:



Higher temperatures favor reactions (2) and (3); at temperatures above 285°C, carbide formation is accompanied by deposition of large quantities of free carbon. The rate of reaction (1) falls off as successive layers of nickel carbide increasingly obstruct the access of CO to the nickel substrate, (see fig. 2). It may further be observed that patches of free carbon may also hinder the progress of the reaction.

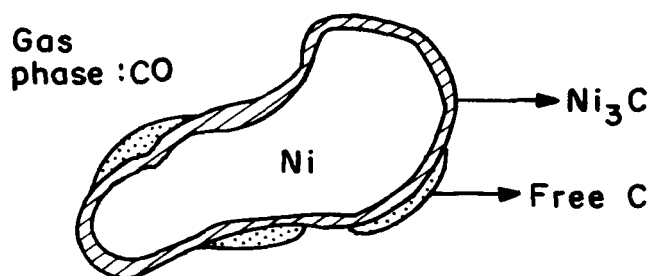


Figure 2.— Reaction of CO with Ni.

Table 2 is a list of the leached alloys that were carbided during this quarter. The duration of treatment and the figures for the total carbon and free carbon, as determined by chemical analysis in each case, are included in the table. X-ray diffraction patterns of these preparations were of little value in identifying the products. A separate study was started in an attempt to evaluate the x-ray patterns (see section F). A finely pulverized Raney nickel (36C) was carbided in an attempt to prepare a material of lower bulk density. Fresh lots of Co_2C , Ni_3C , and carbides of 1Ni-1Co and 1Ni-1Ag (33C, 35C, 42C, and 43C) were prepared to replenish our dwindling stock.

C. Preparation of Nitrocarbides

An interesting property of the transition metals is their ability to form interstitial compounds containing both carbon and nitrogen (5). Thus when $\chi\text{-Fe}_2\text{C}$ is treated with ammonia, nitrogen replaces carbon in the carbide lattice producing chi iron nitrocarbide. When sufficient nitrogen is added to produce instability in the chi structure, transformation to the epsilon iron nitride occurs.

The nitrocarbides of the transition metals and their alloys were prepared by passing gaseous ammonia over the carbides at 260°C at an hourly space velocity of 1000. The duration of treatment for the various carbides and the amount of nitrogen thus incorporated is given in table 3. Fresh lots of nitrocarbides of Co, Ni, and of 1Ni-1Co alloy (21NC, 23NC, and 28NC) were prepared to replenish stocks of these materials.

D. Miscellaneous Preparations

(a) Carbided and nitrocarbided nickel plaque - A 6" x 6" porous plaque of nickel (80069-61, Clevite Corp., Cleveland, Ohio) was sent to this laboratory by Dr. Giner of Tyco Laboratories to be cut into strips and carbided. Inquiries from the manufacturers revealed that although the manufacture of this particular grade of nickel plaque has been discontinued, Ni8512R of 30 mils thickness, currently under production, is practically identical with it and may, in the event of a future need, be used interchangeably.

TABLE 2.- Preparation of carbides

Carbiding gas ----- CO
 Hourly space velocity - 100

Run No.	Charge ^{1/}	Duration of carbiding, hrs.	Temperature, °C	Chemical analysis, weight percent	
				Total C	Free C
25C	RAL-1	13	170-225		
	(1Ni-1Co)	216	250	9.78	6.18
26C	RAL-2	13	170-228		
	(1Ni-3Co)	144	250	8.86	4.86
27C	RAL-3	13	170-225		
	(3Ni-1Co)	144	250	9.33	7.48
29C	RAL-4	5	170-230		
	(1Ni-3Ag)	104	250	1.21	0.7
30C	RAL-5	6	160-220		
	(1Ni-1Ag)	102	250	2.31	1.12
	60-250 mesh				
31C	RAL-5	6	160-220		
	(1Ni-1Ag)	100	250	2.04	1.06
32C	RAL-6	5	160-220		
	(3Ni-1Ag)	102	250	3.42	0.8
33C	RC-1	26	160-240		
	(Raney Co)	72	250	3.59	0.54
34C	RAL-9	5	160-220		
	(3Co-1Ag)	105	250	4.67	1.75
35C	RN-2B2	22	160-220		
	(Raney Ni)	72	250	10.78	6.55
36C	RNL-4	11	160-220		
	(Raney Ni, <mesh)	72	250		
38C	RAL-7	6	160-220		
	(1Co-3Ag)	100	250	1.82	0.72
39C	RAL-8	13	160-230		
	(1Co-1Ag)	100	250	2.56	0.66
40C	RAL-10	13	160-230		
	(1Ni-1Co-1Ag)	100	250	0.84	0.33
41C	RAL-11	22	160-220		
	(1Ni-1Co-1Au)	102	250		
42C	RAL-1	21	160-220		
	(1Ni-1Co)	101	250		
43C	RAL-5	4	160-250		
	(1Ni-1Ag)	102	250		
44C	RAL-12	4	160-250		
	(1Ni-1Ag-1Au)	103	250		

^{1/} Mesh size 150-250, unless otherwise stated.

TABLE 3.- Preparation of nitrocarbides

		Nitriding gas -----	NH ₃		
		Temperature -----	260 °C		
		Hourly space velocity -----	1000		
Run No.	Charge	Duration of nitriding, hrs	Chemical analysis, weight-percent		
			N	Total C	Free C
11NC	19C (Ni ₃ , trace of Ni)	15	1.08		
12NC	20C (Co ₂ C, α-Co, Cub. Co)	39	0.90	5.33	2.50
13NC	26C (Carbided 1Ni-3Co)	48	0.92	8.88	4.50
15NC	27C (Carbided 3Ni-1Co)	48	1.01	9.30	6.38
16NC	25C (Carbided 1Ni-1Co)	48	0.87	9.45	6.46
17NC	29C (Carbided 1Ni-3Ag)	48			
18NC	30C (Carbided 1Ni-1Ag, 60-250 mesh)	48			
19NC	31C (Carbided 1Ni-1Ag, 150-250 mesh)	48			
20NC	32C (Carbided 3Ni-1Ag)	58			
21NC	33C (Co ₂ C, α-Co)	48			
22NC	34C (Carbided 3Co-1Ag)	48			
23NC	35C (Ni ₃ C)	48			
24NC	36C (Ni ₃ C, <250 mesh)	48			
25NC	38C (Carbided 1Co-3Ag)	48			
26NC	39C (Carbided 1Co-1Ag)	48			
27NC	40C (Carbided 1Ni-1Co-1Ag)	48			
28NC	42C (Carbided 1Ni-1Co)	48			
29NC	41C (Carbided 1Ni-1Co-1Au)	48			
30NC	44C (Carbided 1Ni-1Ag-1Au)				

28C - The nickel plaque was cut into four strips of 1 cm width and one of 15/16" width, the length being 6" in each case. The strips were fastened as a unit, separated by stainless steel spacers. The assembly was reduced in a stream of hydrogen at 450°C for 10 hours, and then carbided with carbon monoxide flowing at a rate of 3 liters per hour. As usual, the temperature of the assembly was raised slowly, in steps, to 250°C at which temperature the carbiding was continued for 103 hours.

14NC - Two of the carbided nickel strips were nitrided with anhydrous ammonia. The flow rate of NH_3 was maintained at 30 liters per hour and the treatment lasted for 48 hours at 260°C. The product showed a nitrogen content of 0.39 percent by weight.

(b) Carbides and nitrocarbides of nickel and cobalt obtained from formates, acetates, hydroxides, and butyrates of the metals - In addition to examining the carbides and nitrides of the transition metals and their alloys obtained by the Raney method, research has been extended to studies with interstitial compounds prepared from finely divided metals obtained from their hydroxides and organic salts. Accordingly, the following materials have been prepared:

1. Hydroxides of nickel and cobalt and coprecipitated hydroxides of nickel and cobalt (3Ni-1Co) were prepared by precipitation from aqueous solutions of their sulfates with NaOH. The precipitates were washed free from soluble salts. After drying at 110°C, the mass was crushed to a fine powder which will be reduced with hydrogen and then carbided and nitrided.

2. Cobalt butyrate was prepared according to the directions of Amiel and Moreau (6). The butyrate, on decomposition, is known to give finely divided cobalt of very high surface area (7).

3. A quantity of nickel formate has been reduced to metallic nickel with hydrogen at 450°C.

4. Nickel formate and cobalt acetate was stirred separately in water and the clear solution of cobalt acetate was poured into the suspension of nickel formate. The mass (3Ni-1Co) was taken slowly to dryness and the residue crushed to a fine mix. The preparation will be reduced with hydrogen and the mixed metals so obtained will be carbided and nitrided.

E. Preparation of Nitrides of Nickel and Cobalt

Efforts to prepare nitrides of nickel and cobalt by the customary method of treating finely divided samples of metals with anhydrous ammonia at elevated temperatures were fruitless (8). A brief review of our efforts to prepare the nitrides of nickel and cobalt by some unorthodox methods is presented here. The results were negative. Further efforts are in progress.

The carbides of nickel and cobalt are known to be stripped of carbidic carbon on treatment with hydrogen at 180°-230°C (4,9). The possibility that the resultant metal may be amenable to nitriding on treatment with NH_3 led to the following experiment. Ten grams of Ni_3C was treated with a stream of hydrogen at 260°C for 24 hours at a space velocity of 1000 hr^{-1} . X-ray analysis of the residual material indicated it to be pure nickel. It was then treated with NH_3 at 350°C for 72 hours at an hourly space velocity of 1000. X-ray and chemical analysis of the product so obtained, however, revealed no evidence for the formation of Ni_3N .

In another series of experiments, the possibility of nitriding nickel by treatment with liquid ammonia in a pressurized vessel was investigated. Ten grams of reduced Raney nickel and an excess (150-160 ml) of liquid NH_3 were charged in a stainless steel vessel, fitted with a pressure gauge, and treated in four separate experiments as follows:

1. Kept at room temperature for 72 hrs (gauge pr. 180 psig)
2. Heated in a water bath at 100°C for 14 hrs (gauge pr. 810 psig)
3. Heated in a water bath at 100°C for 81 hrs (gauge pr. 830 psig)
4. Heated in an oil bath at 115°-118°C for 5 hrs (gauge pr. 780-820 psig).

Analysis of the gas from the vessel indicated partial decomposition of NH_3 to N_2 and H_2 . The ammonia and its decomposition products were released from the vessel and the solid removed under an inert atmosphere. Chemical analyses of the powders indicated some slight incorporation of nitrogen. Further work is in progress. The nitrogen content of these preparations are as follows:

1. $0.69 \pm 0.01\%$ nitrogen
2. 0.57 ± 0.01 "
3. 0.64 ± 0.02 "
4. 1.05 ± 0.02 "

F. X-ray Diffraction Study of Transition Metal Alloys

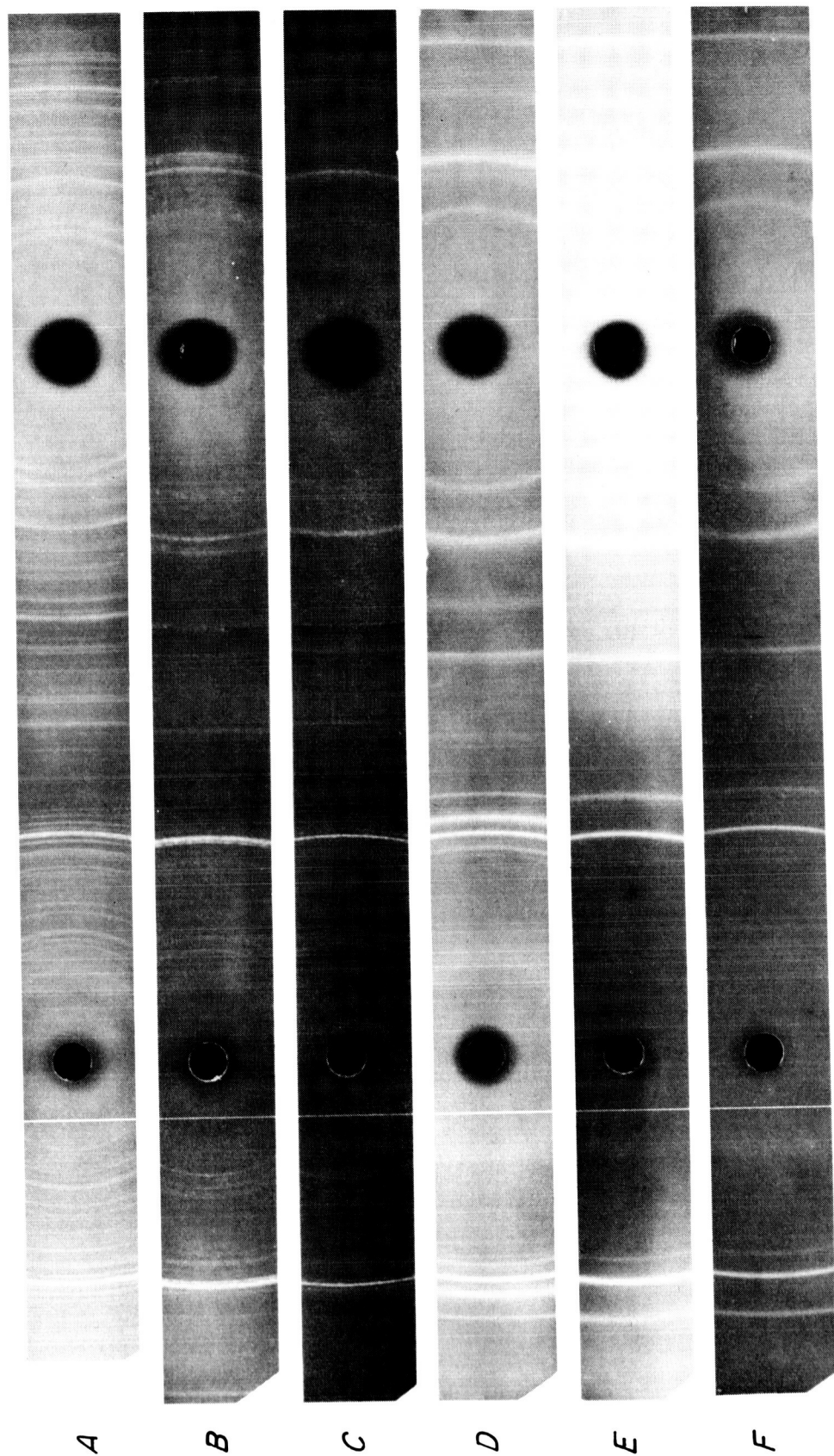
The present diffraction study was originated in an attempt to explain and overcome some problems encountered in the x-ray identification of carbide preparations.

As long as the catalyst consisted of one compound, two compounds of different crystal structure, or two compounds of similar crystal structure but different scattering factors, there was no problem. When preparative work on alloys was started it was found that:

1. There was a lack of information on ternary systems.
2. It was difficult to distinguish compounds with similar structure and scattering factors.

The aluminum-nickel-cobalt system was the first to be tried. A melt of 60Al-20Ni-20Co, RA-1, was made. The Raney alloy was then leached and reduced, RAL-1. A powder photograph was taken, figure 3. The leached and reduced alloy was then carbided (table 2, Run 25C) with pure carbon monoxide. From previous studies on the individual systems, Al-Co, Al-Ni, it was expected that a mixture of cobalt carbide and nickel carbide would be produced. X-ray could only identify the nickel carbide phase. Physical mixtures of cobalt carbide and nickel carbide were prepared to ascertain if their powder patterns could be used in the identification of the carbide phases obtained from the leached Raney alloys. Unfortunately it was as difficult to distinguish these as it was the carbided RAL-1. The similar scattering factors of the nickel and cobalt carbides caused a superimposing of lines and produced a hazy pattern impossible to interpret.

At this point it was decided to temporarily put aside the carbide problem and delve into the nature of the ternary melts before and after leaching. If one compares the patterns of Raney nickel and Raney cobalt with the ternary melt RA-1 (60Al-20Ni-20Co), it is obvious that the melt is not a mixture. Raynor and Pfeil (10) reported that this ternary system consists of solid solutions primarily between Co_2Al_9 and NiAl_3 . A solid solution is distinguished from compound formation in alloys by the similarity in pattern of the solid solution to one of its components, whereas in compound formation a different structure will occur. The films show that the melt is actually a solid solution similar in structure to the Raney cobalt.



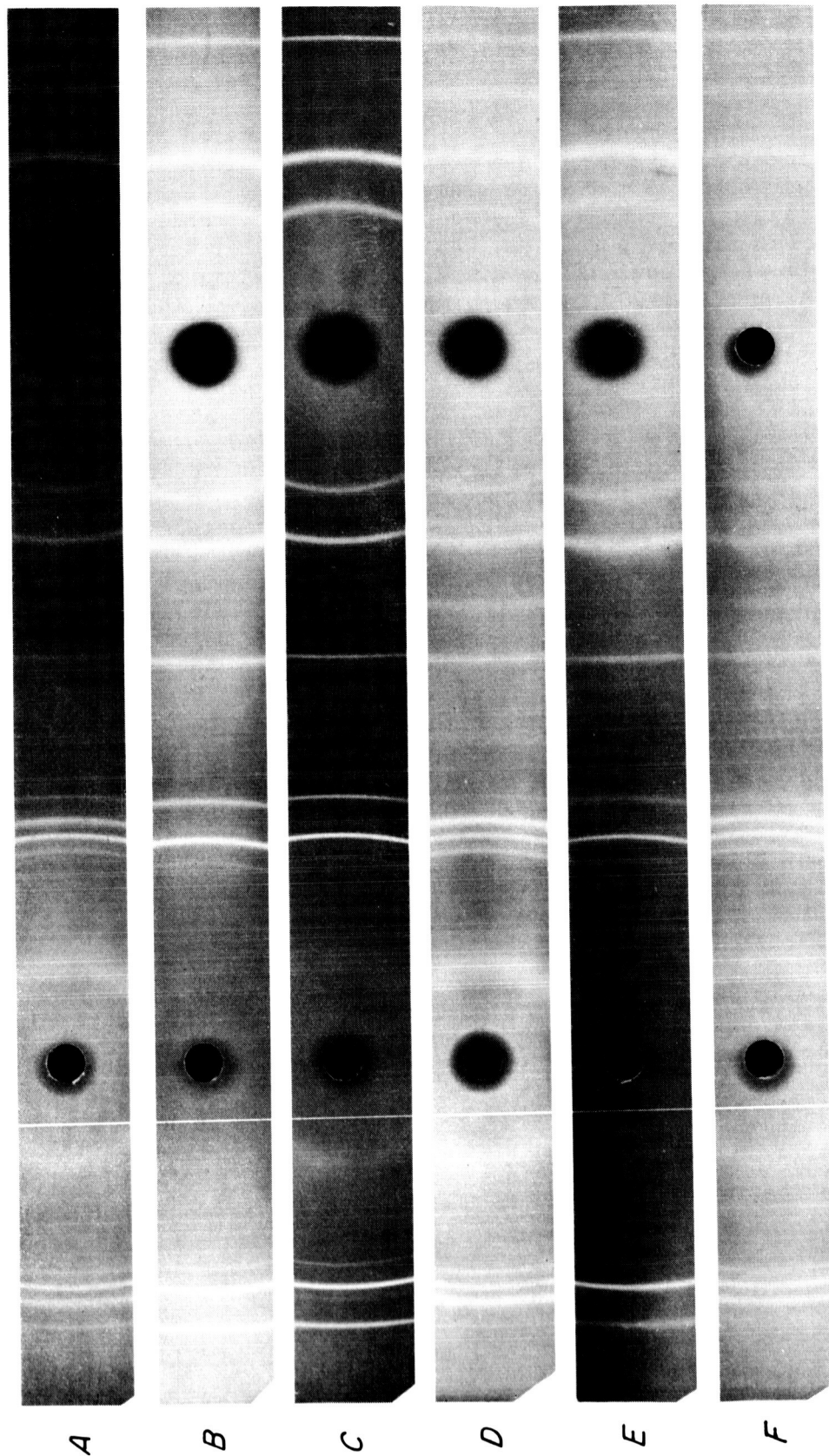
A Raney nickel
B Raney cobalt
C Melt of 60 Al-20 Co
D Mixture of 1 Ni-1 Co
E Leached, reduced Raney alloy of 1 Ni-1 Co
F Melt of 1 Ni-1 Co

Figure 3.—X-ray diffraction powder pattern of the Ni-Co system.

Now if one compares the ternary melt's pattern with the leached and reduced melt (RAL-1) it is obvious that we have a new and distinct species present after leaching. To identify RAL-1 it was decided to compare it with a physical mixture of one part nickel and one part cobalt by weight. The mixture shows both the face-centered cubic structure of nickel and the hexagonal structure of cobalt. This negates the possibility of a mixture since the lines of RAL-1 have been indexed and fit the face-centered cubic structure, table 4 and figure 3. The lattice parameter, $a = 3.528$, of RAL-1 was computed from the individual reflections and averaged but not extrapolated to the value for an angle of 90° , as in normal practice, with the resulting error of 1 part in 350 being present in the final parameter.

RAL-1 was then compared with a 1Ni-1Co alloy, prepared from spectrographically standardized Ni and Co rods, table 4. It was known that nickel and cobalt form a series of continuous solid solutions throughout the entire phase diagram (11). Taylor has showed that at this composition the solid solution was entirely in the nickel crystal structure except for a slight expansion in lattice parameters which increases with increasing cobalt composition (12). Our 1Ni-1Co alloy compared favorably with Taylor's work. Densitometer readings were done on both RAL-1 and the 1Ni-1Co alloy and the relative intensities computed. Table 5 shows the relatively close agreement between the interplanar spacings (d values) and the relative intensities (I/I_1) of the individual lines. Although there are small differences between these two sets of data, one should note that the RAL-1 with its aluminum leached out would be expected to have a slightly expanded structure as compared with the pure 1Ni-1Co alloy due to their drastically different modes of preparation. The lattice parameters, table 4, and the interplanar space are consistent with this conclusion. The marked difference between the I/I_1 values for the third and fourth lines may be explained by the amount of impurities in RAL-1, which are considerable compared with the standard alloy prepared from spectrograde metals.

If the hypothesis was correct for RAL-1 it should work equally well for RAL-2 and RAL-3, table 4. Alloys of 1Ni-3Co and 3Ni-1Co were prepared for comparison with the corresponding leached and reduced Raney's. As one can see from figure 4 and table 4, the agreement with the hypothesis fits at least qualitatively for the 3Ni-1Co alloy and the RAL-3, both being in the face-centered crystal structure. However the 1Ni-3Co alloy is a hexagonal structure whereas the RAL-2 is cubic. Taylor's work helps to explain this latter ambiguity. Taylor (12)



A Mixture of 1 Ni-3 Co
B Leached, reduced Raney alloy of 1 Ni-3 Co
C Melt of 1 Ni-3 Co
D Mixture of 3 Ni-1 Co
E Leached, reduced Raney alloy of 3 Ni-1 Co
F Melt of 3 Ni-1 Co

Figure 4.— X-ray diffraction powder pattern of the Ni-Co system.

TABLE 4.- Crystal structure of nickel-cobalt preparations

Sample	Composition, weight-percent			Treatments		Lattice parameters	Crystal structure
	Ni	Co	Al	No. of leachings	No. of reductions		
Matthey spectro-grade: Ni	99.9999	trace	trace				f.c. cubic
Co	trace	99.9999	trace				hexagonal
Raney cobalt		40.0	60.0	2	1		
Raney nickel	42.0		58.0	2	1		
RAL-1	43.5	54.5	2.00	2	1	$a = 3.528 \text{ \AA}$	f.c. cubic
RAL-2	22.8	75.6	1.55	2	1		f.c. cubic
RAL-3	72.5	25.0	2.35	2	1		f.c. cubic
1Ni-1Co alloy	50.01	49.99	trace			$a = 3.522 \text{ \AA}$	f.c. cubic
1Ni-3Co alloy	25.01	74.99	trace				hexagonal
3Ni-1Co alloy	74.99	25.01	trace				f.c. cubic

TABLE 5.- Comparison of interplanar spacings and
relative intensities of leached
Raney Ni-Co and Ni-Co alloys

Leached and reduced Raney Ni-Co alloy (RAL-1)			1Ni-1Co alloy	
<u>d</u>	<u>I/I₁</u>	<u>Line No.</u>	<u>d</u>	<u>I/I₁</u>
2.0358 ^o A	100.0	1	2.0319	100.0
1.7654	34.1	2	1.7501	38.6
1.2443	42.9	3	1.2436	35.9
1.0638	64.5	4	1.0623	51.4
1.0199	27.5	5	1.0179	27.3

stated that in the series of Ni-Co alloys containing 21.7 percent Ni, 23.4 percent Ni, and 25.9 percent Ni, there was no one stable crystal structure. The structure varied from entirely cubic, to equal amounts of cubic and hexagonal, and to entirely hexagonal. He further stated that the hexagonal and cubic structures coexist above 70 percent cobalt showing no steady trends, but rather that the hexagonal structure tends to appear suddenly in the region of NiCo_3 and to be present in the various cobalt rich-alloys in random quantities. This could explain the inconsistency between the RAL-2 and the 1Ni-3Co alloy.

Conclusions can not be made on these data until a quantitative comparison between lattice parameters, interplanar spacings, and relative intensities have been made. These are presently in the process of being done and will be reported in the next quarter. It will also be interesting to see if this unique phenomenon exists in other leached and reduced ternary systems.

Work Plan

Alloys containing Pd, Ag, and Au in binary and ternary combination with Fe, Co, and Ni will be prepared by the Raney method, and the carbides and the nitrocarbides of the alloys synthesized.

Efforts to prepare nitrides of the transition metals will continue. An apparatus is under construction to study the interaction of anhydrous ammonia with finely divided nickel in a corona discharge.

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^{a/} Titles enclosed in parentheses are translations of the original titles.

APPENDIX I

Samples shipped to Tyco Laboratories this quarter ---	41
Samples shipped to Tyco Laboratories to date -----	87
Samples shipped to non-cost users this quarter -----	114
Samples shipped to non-cost users to date -----	114

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U.S. Army Electronics R&D Labs.
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